

**PROCESS AND APPARATUS FOR REMOVING CHLORIDE AND SODIUM  
IONS FROM AN AQUEOUS SODIUM CHLORIDE SOLUTION**

**Field of the Invention**

5           The present invention relates to a process and apparatus for reducing sodium chloride concentration from an aqueous sodium chloride solution, such as sea water or brine, by removing chloride and sodium ions. More particularly, the present invention discloses a process and apparatus, wherein chloride and sodium ions are removed from the aqueous sodium chloride solution and may be used in subsequent processes. The  
10       sodium may be collected and used in the production of power from a sodium-air fuel cell and chlorine gas may be neutralized with the sodium hydroxide produced in the sodium – air fuel cell to produce sodium hypochlorite.

**Background of the Invention**

15           Water is a precious and life sustaining liquid. Over 97% of the world water supplies are tied up in the ocean. The remaining 3% of the water exists as fresh water supply in natural and man-made lakes and the polar ice caps. With the looming environmental catastrophe brought upon by the global warming there is already a shortage of fresh water supply in the world. Many of the developing countries are  
20       suffering from the failure of the monsoon and consequently the supply of fresh water in reservoirs. The global warming is causing the ice caps to recede thereby melting the fresh water supplies at the polar ice caps into the water that runs into the oceans. While fossil fuels themselves are dwindling and wars have been waged to control the remaining

residues it is possible to foresee a day when wars will be fought for control of fresh water supplies. The danger is not in any future date but can happen within our generation. .

The general approaches for addressing water shortages can be categorized in terms of three basic strategies: conservation, identifying new sources of freshwater and  
5 converting brackish water to freshwater. The goal of water conservation is to promote responsible usage of water. Water conservationists seek to obtain the maximum benefit from existing freshwater sources through the encouragement of responsible usage practices. Although water conservation is clearly beneficial, it is unlikely that it alone will meet the growing water needs of the world.

10 The identification of new sources of freshwater involves searching for new aquifers, typically to supply the growing needs of a particular region as it develops or expands. New technologies permit geologists to search deeper into the earth for water and to search in regions that were previously inaccessible. Other strategies for obtaining freshwater from new sources include extracting water from icebergs or the polar icecap.  
15 More controversially, growing regions with few local water resources are seeking a redistribution of the available resources through water transportation. The southwestern states, for example, have inquired into the possibility of shipping water from the Great Lakes to meet their water needs. Although the search for new freshwater resources will continue and new sources will be identified, it is clear that freshwater is a finite resource  
20 that is politically contentious and that the most accessible sources have already been located and tapped and are being consumed. Future sources will become increasingly expensive to both locate and utilize.

A third strategy, water conversion, seeks to produce freshwater from brackish water in an attempt to exploit the vast potential of the world's oceans. Water conversion is most commonly practiced today in arid regions, such as the Middle East, where little or no freshwater resources are naturally available. Conversion of brackish water to  
5 freshwater involves a desalination process in which freshwater or purified water is separated or extracted from brackish water. There are a variety of methods available already to convert brackish water into potable water. Evaporation and condensation, reverse osmosis, and electrodialysis are some of the very common techniques.

A common desalination process in use today is based on reverse osmosis, a  
10 separation method that uses pressure to induce diffusion of pure water from brackish water through a semi-permeable membrane to provide pure water on one side of the membrane and concentrating salts and impurities on the other side of the membrane. Although reverse osmosis is an effective desalination technique, it is slow, expensive and requires high energy consumption. Related techniques, such as electrodialysis, show  
15 improved energy efficiency, but nonetheless remain costly, especially for high volume throughputs. Reverse osmosis and electrodialysis work very well with salt content under 60,000 ppm. Anything more than that, such as sea water that may have salt content of 350,000 ppm, would require higher pressures (close to 1000 psi) and the current membranes, in addition to being expensive cannot sustain such high pressures.

20 Evaporation/distillation is the preferred method. It is somewhat expensive but work is being performed to continuously decrease the cost by efficient designs.

The current invention overcomes deficiencies in the prior art and provides a novel process and apparatus for the reduction of salt content from aqueous sodium chloride,

such as brine, which incorporates a system that electrolytically dissociates NaCl into chlorine gas and sodium metal. Preferably, the system is powered by solar energy.

Further, the sodium may be collected and used to fuel a sodium-air fuel cell that produces power and produces sodium hydroxide. The sodium hydroxide may then be reacted with

5 the chlorine gas to produce sodium hypochlorite, which is an industrial bleach.

### Summary of the Invention

The present invention discloses a process for removing salt (NaCl) from an aqueous sodium chloride solution, such as seawater or brine. The process includes

10 electrolyzing an aqueous sodium chloride solution to remove chloride and sodium ions in the form of chlorine gas and sodium metal. Typical electrolysis of a sodium chloride

solution will produce chlorine at the anode and hydrogen at the cathode. The process of the present invention on the other hand, utilizes electrode materials that facilitate the production of chlorine gas and inhibit the evolution of hydrogen from the aqueous

15 sodium chloride solution. The sodium cations are deposited onto a metal surface having a high hydrogen overpotential. Since the hydrogen overpotential is high at this surface,

the cell voltage has to be raised sufficiently high to produce any hydrogen. However at these potentials sodium cations deposit to produce sodium metal. For example, if the

chosen substrate for cathode is mercury, the sodium deposits on mercury forming sodium

20 amalgam. The sodium metal is transported to and coupled against an air depolarizing

cathode to form a metal-air fuel cell to produce power. Initially the cell is started with some low concentration of sodium hydroxide. However the product of the reaction

between the sodium amalgam and the air electrode of the fuel cell being sodium

hydroxide, it is possible to react the sodium hydroxide with the chlorine gas to produce sodium hypochlorite.

An embodiment of the present invention discloses a process for lowering the sodium chloride concentration in an aqueous sodium chloride solution, as well as, making sodium hypochlorite and producing electrical power. The process includes electrolyzing a source of aqueous sodium chloride solution, such as brine, in a first container. The electrolysis splits sodium chloride in the aqueous sodium chloride solution, which produces chlorine gas, sodium metal and processed solution. The sodium cations are collected on a surface, such as a metal surface coated with a material having a high hydrogen overpotential, and removed from the first container. The aqueous sodium chloride solution having depleted NaCl content is then collected and may be utilized as is or further processed to remove contaminants. The amalgamated surface may be coupled to an air depolarizing electrode to form a metal-air fuel cell in a second container containing dilute sodium hydroxide to anodically dissolve the sodium metal from the amalgam in the water thereby extracting electrons and producing more concentrated sodium hydroxide and electrical power. The electrons from the anodic dissolution of sodium metal flow through the external circuit to the cathode of the fuel cell, where oxygen reduction occurs. The sodium hydroxide from the second container is flowed to a third container where the chlorine gas from the first electrolysis cell is bubbled thereby producing sodium hypochlorite.

The electrolysis above may comprise applying an electric potential across an anode and a cathode, wherein the anode is in contact with the aqueous sodium chloride solution. Chlorine evolution will take place at the anode. Since chlorine is a reactive gas,

graphite, or lead dioxide coated graphite or platinum or DSA type of electrode substrates are preferable. Preferably, the electrodes are  $\text{RuO}_2$  coated titanium electrodes. Chlorine is evolved at the anode. The sodium cations are deposited at the mercury-coated surface, and forms sodium amalgam at the surface. Preferably, the process includes restricting the flow of dissolved chlorine gas to the cathode. In a preferred embodiment, a membrane is disposed in the first container between the anode and the cathode. The membrane restricts the flow of dissolved chlorine to the cathode, i.e. amalgamated surface, while permitting sodium ions to permeate through. In the absence of the membrane, the dissolved chlorine will react with the mercury surface producing passivating film of mercurous chloride.

In a preferred embodiment, the electric potential for the process is supplied by a photovoltaic device in electrical communication with the anode and the cathode. The photovoltaic device may comprise at least one triple junction solar cell, which may be at least one triple junction amorphous silicon solar cell.

In a preferred embodiment, the process incorporates a stainless steel belt coated with mercury acting as the cathode surface. Mercury coating of stainless steel may be performed using traditional electroplating process using appropriate pre-treatment steps. The stainless steel belt may be adapted to move from the first container into the second container where the belt is coupled to the fuel cell. Preferably, a recirculating stainless steel belt is adapted to continually flow in a repeating route between the first container and the second container.

An embodiment of the disclosed process produces processed solution having a sodium chloride concentration lower than the sodium chloride concentration of the source

of aqueous sodium chloride solution by splitting and removing chloride anions and sodium cations. The processed solution may be discharged from the first container and further processed to produce fresh water for human consumption or agricultural use.

An embodiment of the present invention discloses an apparatus lowering the sodium chloride concentration in an aqueous sodium chloride solution, as well as, making sodium hypochlorite and producing electrical power. The apparatus of the present invention uses a source of electrical energy for electrolyzing a source of aqueous sodium chloride solution, such as brine, contained in a first container, an electrolyzer in electrical communication with the source of electrical energy splits sodium chloride in the aqueous sodium chloride solution resulting in chlorine gas, and sodium amalgam and processed solution. A sodium collector collects sodium on a mercury coated surface and transports the sodium from the first container to a second container containing dilute sodium hydroxide and an air depolarizing fuel cell electrode. The aqueous sodium chloride solution having the NaCl removed is then collected from the first container and may be utilized as is or further processed to remove other contaminants. The fuel cell electrode is coupled to the amalgamated surface in said second container, which dissolves the sodium amalgam in dilute sodium hydroxide to produce concentrated sodium hydroxide and electrical power. This power may be utilized to subsidize the overall power requirement of the electrolysis system, such as operation of the belt or the electrolysis itself. The sodium dissolves in the water producing electrons through the external circuit to the cathode of the fuel cell, where oxygen reduction occurs. The sodium hydroxide from the second container is allowed to flow to a third container where the sodium hydroxide reacts with the chlorine gas producing sodium hypochlorite. A first conduit is

used to flow the sodium hydroxide from the second container to a third container. The sodium hydroxide from the second container is flowed to a third container where the sodium hydroxide reacts with the chlorine gas producing sodium hypochlorite.

In a preferred embodiment, the source of electrical energy is a photovoltaic device  
5 for converting solar energy to electricity. The photovoltaic device may comprise at least one triple junction solar cell, preferably at least one triple junction amorphous silicon solar cell.

In a preferred embodiment, the electrolyzer comprises an anode in electrical communication with the source of electrical energy and in contact with the source of  
10 aqueous sodium chloride solution and a cathode in electrical communication with the source of electrical energy. The source of electrical energy generates an electric potential between the electrodes and the said anode liberates chlorine ions from the aqueous sodium chloride solution and the chlorine ions combine to produce the chlorine gas. The cathode, i.e. amalgamated surface, contacts and collects the sodium cations. In a  
15 preferred embodiment, a membrane is disposed in the first container between the anode and the cathode, wherein the membrane inhibits the flow of dissolved chlorine to the cathode.

In a preferred embodiment, the sodium collector is a stainless steel belt coated with a material having a high hydrogen overpotential, such as mercury, tin or lead. The  
20 stainless steel belt may comprise a recirculating stainless steel belt adapted to flow from the first container to the second container, wherein the recirculating stainless steel belt collects the sodium metal in the first container, flows to the second container and contacts the dilute sodium hydroxide in the second container to release the sodium as sodium



cations and releasing electrons. The electrons flow through the external circuit to the cathode and reduce oxygen from the air to produce hydroxyl ions. The stainless steel belt may comprise a recirculating stainless steel belt adapted to continually flow in a repeating manner between the first container and the second container.

5           The disclosed apparatus produces processed solution having a sodium chloride concentration lower than the sodium chloride concentration of the source of aqueous sodium chloride solution by splitting and removing chloride ions and sodium cations. The processed solution containing depleted sodium chloride content may be discharged from the first container through an outlet and collected and further processed to produce  
10   fresh water for human consumption or agricultural use.

          An embodiment of the present invention provides a process and apparatus for electrolyzing aqueous sodium chloride solution to reduce sodium chloride content, fueling a sodium-air fuel cell with sodium liberated from the aqueous sodium chloride solution and producing sodium hypochlorite.

15           An embodiment of the present invention provides a process and apparatus for electrolyzing aqueous sodium chloride solution to remove chlorine and sodium ions from the aqueous sodium chloride solution to reduce the salt (NaCl) content of the aqueous sodium chloride solution.

          An embodiment of the present invention provides a process and apparatus for  
20   electrolyzing aqueous sodium chloride solution to produce chlorine gas and sodium metal, substituting the evolution of hydrogen gas at the cathode surface.

          An embodiment of the present invention provides a process and apparatus for electrolyzing aqueous sodium chloride solution, wherein sodium liberated from the

electrolysis of the aqueous sodium chloride solution is deposited on a moving stainless steel belt, which has been coated with a material having high hydrogen overpotential, such as mercury.

An embodiment of the present invention provides a process and apparatus for electrolyzing, wherein sodium liberated from the electrolysis of the aqueous sodium chloride solution is deposited on a moving stainless steel belt, wherein the stainless steel acts as a cathode.

An embodiment of the present invention provides a process and apparatus for electrolyzing aqueous sodium chloride solution, wherein sodium liberated from the electrolysis of the aqueous sodium chloride solution is deposited on a moving stainless steel belt, wherein the moving stainless steel belt removes sodium from the cathode vicinity that exposes fresh surface for more sodium to be deposited.

An embodiment of the present invention provides a process and apparatus for electrolyzing aqueous sodium chloride solution, wherein sodium liberated from the electrolysis of the aqueous sodium chloride solution is deposited on a moving stainless steel belt to produce sodium amalgam, wherein the sodium amalgam is coupled against an air depolarizing fuel cell electrode.

An embodiment of the present invention provides a process and apparatus for electrolyzing aqueous sodium chloride solution, wherein sodium liberated from the electrolysis of the aqueous sodium chloride solution is used to produce a sodium-air fuel cell which produces power, wherein the power may be used to move the belt or do other useful work such as processing the processed solution further to produce potable water.

An embodiment of the present invention provides a process and apparatus for electrolyzing aqueous sodium chloride solution to produce sodium hypochlorite, wherein sodium liberated from the electrolysis of the aqueous sodium chloride solution is used to fuel a sodium-air fuel cell that reacts to produce sodium hydroxide and wherein chlorine  
5 gas liberated from the electrolysis of the aqueous sodium chloride solution reacts with the sodium hydroxide from the sodium-air fuel cell to produce the sodium hypochlorite.

### **Brief Description of the Drawings**

In order to assist in the understanding of the various aspects of the present  
10 invention and various embodiments thereof, reference is now be made to the appended drawings, in which like reference numerals refer to like elements. The drawings are exemplary only, and should not be construed as limiting the invention.

Figure 1 is a fragmentary, cross-sectional view of a tandem or cascade photovoltaic device comprising a plurality of p-i-n-type cells, each layer of the cells  
15 formed from an amorphous silicon alloy material;

Figure 2 is an illustration of desalination apparatus for use with an embodiment of the process of the present invention;

Figure 3 is a block diagram of an embodiment of the process of the present invention, wherein chlorine and sodium ions are removed from aqueous sodium chloride  
20 solution to produce processed solution having a sodium chloride concentration less than the aqueous sodium chloride solution;

Figure 4 is a block diagram of an embodiment of the process of the present invention, wherein the chlorine removed from aqueous sodium chloride solution is used to produce sodium hypochlorite and power; and

Figure 5 is an illustration of the splitting of the NaCl in the aqueous sodium chloride solution, wherein a membrane inhibits the chlorine ions from migrating to the cathode, wherein sodium metal is collected by a cathodic belt.

### **Detailed Description of the Invention**

An illustration of an apparatus, generally referred to as **100**, for the production of sodium hypochlorite (NaOCl) power and aqueous hydrogen chloride having a lower concentration of hydrogen chloride than the original source is presented in Figure 2. A preferred embodiment of the instant invention utilizes a renewable source of solar energy, sunlight, to effect the formation of sodium hypochlorite (NaOCl), power and aqueous hydrogen chloride having a lower concentration of hydrogen chloride than the original source. Although sunlight is the preferred source of energy, the electric potential may be supplied by any source of power, such as a generator powered by coal, natural gas or other fossil fuels. Sunlight is collected by a photovoltaic device **102** and converted to electrical energy that is used to produce an electrical potential across electrodes **104** and **105**, which induces the electrolysis of sodium chloride (NaCl). The aqueous sodium chloride solution may be brine. The brine **101** may be a natural source of brine, such as seawater, or the brine may be any NaCl containing water. The brine may be processed at the natural source or the brine may be collected and transported to a facility designed for the processing of the brine. The brine may also include chemically or physically pre-

treated forms of brine. The photovoltaic device **102** may be placed into, on the surface of or adjacent to the source of aqueous sodium chloride solution. The photovoltaic device **102** includes one or more materials that are capable of absorbing solar energy and converting it to electrical energy. The electrical energy produced by the photovoltaic device **102** is provided as an electrical potential to electrodes **104** and **105** that are in contact with the aqueous sodium chloride solution **101**. Preferably, the electrodes **104** and **105** are RuO<sub>2</sub> coated titanium electrodes. The potential between the electrodes **104** and **105** of the photovoltaic device **102** is sufficient to drive electrolysis of NaCl in the brine that liberates chlorine and sodium ions from the aqueous sodium chloride solution.

The aqueous sodium chloride solution may enter the first container **112** by any acceptable means. For example, the aqueous sodium chloride solution may be pumped through an inlet **108** or poured into the first container **112**. The first container **112** may be positioned with respect to the aqueous sodium chloride solution to allow gravity to flow the aqueous sodium chloride solution into the first container. The aqueous sodium chloride solution may enter the first container through an inlet **108** and may exit the first container through an outlet **109**. Preferably, the inlet **108** provides a means of access to the first container **112** for the aqueous sodium chloride solution entering the system to be processed and the outlet **109** provides a means of discharging processed solution to exit the system. The aqueous sodium chloride solution may enter the first container **112** continually or intermittently. To control the desired flow of aqueous sodium chloride solution into the first container, the inlet **108** may be equipped with a valve **114**. Similarly, to control the flow of processed solution out of the first container **112**, the outlet **109** may be equipped with a valve **115**.

Preferably, a membrane **111** is set between the anode **104** and the cathode **105**.

Preferably, the membrane **111** comprises a sodium conducting fluorinated polymer membrane, such as NAFION<sup>®</sup>, wherein the membrane inhibits the flow of dissolved chlorine gas to the cathode **105** as the chlorine gas is liberated by the anode **104** while the sodium cations are free to flow through the membrane **111**, as illustrated in Figure 5. In a preferred embodiment, the membrane **111** is a perfluorosulfonic acid polymer membrane, such as a NAFION<sup>®</sup> membrane. Preferably, the membrane **111** has a thickness of between 0.025 mm and 0.13 mm, depending on the cell resistance.

Preferably, the inlet **108** and outlet **109** are set on opposite sides of the membrane **111** and sodium ions and processed solution flow through the membrane **111** as the chloride ions combine to produce chlorine gas. For example, referring to Figure 2, the system may be designed so that the aqueous sodium chloride solution enters the first container **112** at the top portion of the first container **112** and the processed solution exits the first container **112** at the bottom portion of the first container **112**. This encourages the flow of sodium and remaining processed solution to flow through the membrane. In an alternative embodiment, the outlet **109** may be connected to a pump to force the flow.

As the electric potential is applied across the electrodes **104** and **105**, chlorine gas is liberated at the anode **104** and sodium metal is collected at the cathode **105**. The chlorine gas is emitted from the first container **112**. Preferably, the emission of the chlorine gas occurs on the side of the first container **112** having the inlet **108** and the collection of sodium occurs on the side of the first container **112** having the outlet **109**. The chlorine gas is collected and used at a later point in the process. Preferably, the

chlorine is collected and fed to a third container **130** to react with sodium hydroxide, as described below.

The sodium metal collected by the cathode **105** is transferred to a second container **120**. The cathode **105** may be an amalgamated surface, such as metal coated with a material having a high hydrogen overpotential to avoid the evolution of hydrogen at the cathode **105**. Examples of substrate metal that may be used include but are not limited to stainless steel, titanium and high performance corrosion resistant alloys, such as HASTELLOY®. In a preferred embodiment, a motorized recirculating belt **110** is used to collect and transfer the sodium cations from the first container to the second container, as illustrated in Figures 2 and 5. The optimum speed of the belt will be dependent on the current density and will be set to maximize efficiency. To collect the sodium, the recirculating belt **110** preferably comprises a stainless steel belt amalgamated with a material having high hydrogen overpotential, such as mercury, lead or tin. Mercury is the preferred material due to its high hydrogen overpotential. As the sodium collects on the belt **110** in the first container **112**, the sodium deposits on the surface of the belt **110** to produce sodium amalgam, then the belt **110** carries the sodium amalgam to the second container **120**. To assist in sodium cation deposition, the cell voltage is preferably at least 1.8 V – 2.0 V, depending on current density. For example, at 1000 mA/cm<sup>2</sup> the cell voltage may be about 2.2 V to about 2.4 V. Rollers **124** may be used to maintain the recirculating route of the belt from the first container to the second container. Preferably, the rollers **124** are positioned to not contact the sodium-contacting surface, as illustrated in Figure 2. Although a recirculating belt **110** is preferred, any collection and transfer system may be used. For example, a cathode having the above

noted properties may be dipped into the first container for a time sufficient to attract the sodium, then removed and dipped into the second container to allow the sodium to dissolve in the dilute sodium hydroxide. The electrical contact may be a brush type of contact also.

5           In the second container **120**, the sodium amalgam dissolves in dilute sodium hydroxide and couples against an air-depolarizing cathode **122** located in the second container **120**. As the sodium amalgam dissolves in water molecules in the dilute sodium hydroxide, electrons are released. These electrons flow through the external circuit to the cathode, i.e. air-depolarizing fuel cell **122**, where oxygen reduction takes  
10 place. The combination of sodium metal anode and oxygen cathode will form a metal-air fuel cell. The sodium air fuel cell produces power that may be used to move the belt **110** or other functions. Additionally, this reaction produces concentrated sodium hydroxide, which may be used to neutralize the chlorine gas to produce sodium hypochlorite. The mercury resists dissolving in the second container **120** as the sodium is released and the  
15 belt **110** returns to the first container **112** to collect more sodium. Preferably, the dilute sodium hydroxide is about 0.01M and the concentrated sodium hydroxide has a higher molarity than the dilute sodium hydroxide, as sodium cations react with water in the dilute sodium hydroxide to produce more NaOH molecules and reduce the water content. Pure water may be used in place of the sodium hydroxide, however dilute sodium  
20 hydroxide is preferred. The needs of the system only require that water molecules are available to remove sodium from the cathode. The dilute sodium hydroxide is preferred because the concentrated sodium hydroxide may be reacted with the chlorine gas as detailed below.



A second conduit **131** transfers the concentrated sodium hydroxide from the second container **120** to a third container **130**. A first conduit **132** collects and transfers the chlorine gas emitted from the first container **112** to the third container **130**. A pump may be used to feed the chlorine gas through the first conduit **132** to the third container

5 **130**. In the third container **130**, the chlorine gas is bubbled through the concentrated sodium hydroxide. The chlorine gas reacts with the concentrated sodium hydroxide to produce sodium hypochlorite. The sodium hypochlorite may be collected and processed for commercial purposes.

Unlike traditional water electrolysis, where oxygen gas and hydrogen gas are

10 produced, aqueous sodium chloride electrolysis typically produces hydrogen gas and chlorine gas. In a batch process, if the electrolysis continuously removes chlorides as chlorine gas and sodium ions as sodium metal, the residual aqueous sodium chloride will become weak in salt content. However, a preferred embodiment of the present invention does not evolve hydrogen but removes sodium cations to reduce the salt (NaCl) content.

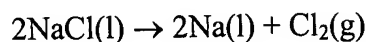
15 The inventors of the present invention have found the evolution of hydrogen at the cathode may be substituted with sodium metal deposition by the proper choice of cathode material.

Hydrogen overpotential on certain metals is very low and in certain metals is very high. For example on platinum surfaces hydrogen overpotential is very low which

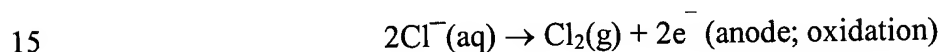
20 indicates that hydrogen evolution is very favorable on this substrate. In contrast, hydrogen overpotential on lead, tin and mercury is high and hence hydrogen evolution is unfavorable. Therefore, to avoid hydrogen evolution during aqueous sodium chloride electrolysis, the cathode material should be a material with high overpotential, such as

lead, tin or mercury. In a preferred embodiment, the cathode material is mercury, the material with a highest overpotential. Since the hydrogen overpotential will be high, the cell voltage will be high (about 1.8 to 2.0 V depending on current density). At the high cathodic potentials, the sodium cations from aqueous sodium chloride will begin to  
5 deposit on the mercury cathode. In effect, aqueous sodium chloride is electrolyzed to produce chlorine and sodium. If the aqueous sodium chloride solution from the electrolysis bath is not changed, gradually there will be a decrease in the NaCl content and a gradual rise in the electrolytic cell resistance since ionic conductivity will be gradually going down with the removal of sodium and chloride ions from the water. At  
10 some point the processed solution can be removed and fresh aqueous sodium chloride solution may be added to continue the process.

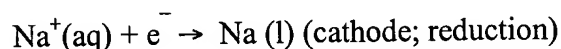
The electrolysis reaction is given by



where the half cell reactions are



and



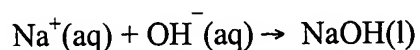
The decrease in salinity as indicated by decrease in conductivity is an indication  
20 to remove the spent electrolyte and replace it with fresh aqueous sodium chloride solution. This conductivity change can be continuously monitored and automatic sensing systems can dump the spent electrolyte and re-supply with fresh electrolyte. The sodium (Na) is deposited onto a coated belt, which is moving continuously in a recirculating

fashion from the first container to the second container, as illustrated in Figures 2 and 5.

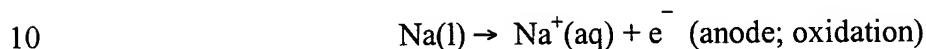
When the belt containing sodium (Na) is moving into the second container it works as an anode against the air electrode. The sodium amalgam-air fuel cell also provides

additional power. Sodium dissolves in water producing electrons, which flow through

5 the external circuit to the cathode where the oxygen reduction takes place. The product is sodium hydroxide (NaOH). The reaction is given by



where the half cell reactions are



and



Chlorine reacts with the sodium hydroxide (NaOH) to form sodium hypochlorite

15 (NaOCl). The reaction is given by

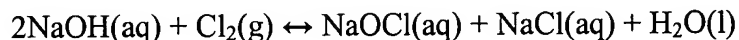


Figure 3 is a block diagram of aspects of a preferred embodiment of the present invention, wherein a photovoltaic device is a source of electrical energy to initiate the  
20 process to produce processed solution having a lower sodium chloride concentration than the source of aqueous sodium chloride solution. Electrodes are placed into contact with a source of aqueous sodium chloride solution **200** and **201**, such as seawater or brine. A source of solar energy **202**, e.g. sun, provides solar energy to the photovoltaic device **203**.

The photovoltaic device provides an electric potential across the electrodes **204**, which induces electrolysis of the sodium chloride **205**. The electrolysis produces chlorine gas and sodium **206**. The chlorine gas bubbles out from the aqueous sodium chloride **208** and the sodium deposit onto a cathode **207**. By removing chlorine and sodium ions,  
5 weak aqueous sodium chloride is produced **209**. Continuation of the electrolysis further reduces the concentration of sodium chloride in the water.

Figure 4 is a block diagram of aspects of a preferred embodiment of the present invention, wherein a photovoltaic device is a source of electrical energy to initiate the process to produce processed solution having a lower sodium chloride concentration than  
10 the source of aqueous sodium chloride solution, to produce power via a sodium air fuel cell and to produce sodium hypochlorite. Electrodes are placed into contact with a source of aqueous sodium chloride solution **300** and **301**, such as seawater or brine. A source of solar energy **302**, e.g. sun, provides solar energy to the photovoltaic device **303**. The photovoltaic device provides an electric potential across the electrodes **304**, which  
15 induces electrolysis of the sodium chloride **305**. The electrolysis produces chlorine ions that combine to produce chlorine gas and sodium cations **306**. Preferably, the chlorine gas bubbles from the aqueous sodium chloride solution **311** and is collected for later use and the sodium is deposited onto an amalgamated surface **307**. The sodium amalgam couples against an air-depolarizing electrode **308**. The sodium air fuel cell produces  
20 power **310** and a byproduct of the coupling is sodium hydroxide **309**. The sodium hydroxide combines with the chlorine gas to produce sodium hypochlorite **312**.

The photovoltaic device preferably utilizes a semiconductor as the active material. A preferred photovoltaic device structure for the instant invention is the n-i-p structure.

This structure consists of an i-type (intrinsic) semiconductor layer interposed between an n-type semiconductor layer and a p-type semiconductor layer. In a typical simple device, a transparent conducting electrode layer is contacted to the p-type layer and a metal electrode is contacted to the n-type layer. In such a device, incident sunlight passes  
5 through the transparent electrode and p-type layer and is absorbed by the i-type layer. Absorption by the i-type layer leads to promotion of electrons from the valence band to the conduction band and to the formation of electron-hole pairs in the i-type layer. The electrons and holes are the charge carriers needed to produce electricity. The adjacent p-type and n-type layers establish a potential in the i-type layer that separates the electrons  
10 and holes. The electrons and holes are subsequently conducted to oppositely charged collection electrodes that provide the potential needed to induce the water splitting reaction.

Representative semiconductor materials suitable for the absorption of solar energy include crystalline silicon, polycrystalline silicon, amorphous silicon, microcrystalline  
15 silicon or related materials, including alloys of silicon with germanium. Other materials such as GaAs, CdS and CuInSe<sub>2</sub> may also be used. These materials can be prepared as n-type, i-type or p-type and have bandgap energies that permit absorption of at least a portion of the solar spectrum. Amorphous silicon is a preferred i-type material in a n-i-p structure because it possesses a direct bandgap and exhibits a high absorption strength  
20 over a wide wavelength range of the solar spectrum. The high absorbance of amorphous silicon is desirable because it leads to efficient absorption of sunlight in thinner devices. Thinner devices require less material and are correspondingly more cost effective.

A variety of n-i-p photovoltaic structures are operable to provide the electrical potential required to effect the water splitting reaction of the instant invention. A basic objective is to use a photovoltaic device structure that maximizes the absorption of solar energy and the conversion efficiency of solar energy to electrical energy. Several

5 strategies for improving the performance of amorphous silicon based photovoltaic devices are possible. These strategies include the use of microcrystalline silicon to form the p-type layer, integration of two or more n-i-p structures to form tandem devices, and inclusion of a back reflector layer in the structure. U.S. Pat. No. 4,609,771, the disclosure of which is hereby incorporated herein by reference, discloses the use of microcrystalline

10 silicon p-type layers in solar cells. The inventors therein demonstrate that microcrystalline silicon has a higher transparency to sunlight than amorphous silicon. As a result, use of a microcrystalline silicon p-type layer allows more incident sunlight to reach the i-type layer and a higher concentration of charge carriers is produced as a result. U.S. Pat. Nos. 4,600,801 and 5,977,476, the disclosures of which are hereby incorporated

15 herein by reference. The strategy associated with tandem devices is to couple multiple n-i-p structures in series in an attempt to harvest as much incident sunlight as possible. Although high, the absorption efficiency of i-type amorphous silicon layers is substantially less than 100%. Placement of a second n-i-p structure directly below the n-i-p structure that is directly incident to the sunlight provides an opportunity to capture light

20 not absorbed by the first n-i-p structure. Tandem structures that include the stacking of three n-i-p structures to form triple cells have also been described. Additional strategies such as bandgap tailoring of the i-layer from one n-i-p structure to the next have also been demonstrated to improve the light harvesting efficiency of tandem structures. In

these strategies, separate n-i-p structures in a tandem structure include i-type layers that are optimized to selectively absorb different portions of the solar spectrum. Amorphous silicon, for example, may be used to absorb the short wavelength portions of the solar spectrum, while SiGe alloys having various amounts of Ge may be used to absorb longer wavelengths since alloying with Ge reduces the bandgap. Representative triple cell structures are described in the following journal publications, the disclosures of which are hereby incorporated herein by reference: “Roll to roll manufacturing of amorphous silicon alloy solar cells with in situ cell performance diagnostics” by M. Izu and T. Ellison (Solar Energy Materials & Solar Cells vol. 78, p. 613 – 626 (2003)) and “Triple-junction amorphous silicon alloy solar cell with 14.6% initial and 13.0% stable conversion efficiencies” by J. Yang, A. Banerjee and S. Guha (Applied Physics Letters, vol. 70, p. 2975 – 2977 (1997)).

Back reflecting layers are reflective layers that are typically deposited directly on the substrate. The role of a back reflecting layer is to reflect any light passing through all of the n-i-p cells stacked in a tandem device. Through this reflection process, light that is initially not absorbed is redirected to the stacked n-i-p devices for a second pass and improved absorption efficiency results. Representative back reflecting layer materials include Al, ZnO, Ag, Ag/ZnO, and Al/ZnO.

An important advantage associated with amorphous silicon is the ability to manufacture it in a large scale continuous manufacturing process. Crystalline silicon, on the other hand, can only be prepared in a slow, smaller scale process because of the slow crystallization processes associated with its formation. Consequently, great efforts have been directed at the large scale production of amorphous silicon. Modern web rolling

processes permit the high speed production of single and multilayer thin films amorphous silicon based devices. The production of amorphous silicon on a continuous web has been previously described in, for example, U.S. Pat. Nos. 4,485,125; 4,492,181; and 4,423,701, and U.S. Appl. Ser. No. 10/228,542 the disclosures of which are hereby

5 incorporated herein by reference.

A p-i-n multiple cell device may be obtained by reversing the order of the n-plus and p-plus layers or regions of the n-i-p multiple cell device described above. Referring to Figure 1, a tandem or cascade-type photovoltaic cell, formed of successive p-i-n layers each including an amorphous silicon alloy material, is shown generally by numeral **10**.

10 The photovoltaic device illustrated in FIG. 1 may be used with the present invention.

Figure 1 shows a p-i-n type photovoltaic device such as a solar cell made up of individual p-i-n type cells **12a**, **12b** and **12c**. Below the lowermost cell **12a** is a substrate **11** which may be transparent or formed from a metallic surfaced foil. The substrate material **11** may be stainless steel, aluminum, tantalum, molybdenum or chrome, as well as substrates  
15 formed of synthetic polymers, glass or glass-like material on which an electrically conductive electrode is applied.

Each of the cells **12a**, **12b** and **12c** include an amorphous semiconductor body containing at least a silicon alloy. Each of the semiconductor bodies include an n-type conductivity region or layer **20a**, **20b** and **20c**; an intrinsic region or layer **18a**, **18b** and  
20 **18c**; and a p-type conductivity region or layer **16a**, **16b** and **16c**. The term "amorphous" as used herein includes all materials exhibiting long-range disorder, regardless of their short or intermediate range order and regardless of whether those materials are otherwise labeled polycrystalline or crystalline. As illustrated, cell **12b** is an intermediate cell and,



as indicated in Figure 1, additional intermediate cells may be stacked atop the illustrated cells.

For each of the cells **12a**, **12b** and **12c**, the p-type and n-type layers of semiconductor material are characteristically light transmissive and highly conductive.

- 5 The intrinsic layers of semiconductor material are characterized by an adjusted wavelength threshold for solar photoresponse, high light absorption, low dark conductivity and high photoconductivity, including sufficient amounts of a band gap adjusting element or elements to optimize the band gap for the particular cell application. Preferably, the intrinsic layers of semiconductor material are band gap adjusted to
- 10 provide cell **12a** with the lowest band gap, cell **12c** with the highest band gap and cell **12b** with a band gap between the other two, as light enters the semiconductor material from the top. However, the intrinsic layers of semiconductor material are band gap adjusted to provide cell **12a** with the highest band gap, cell **12c** with the lowest band gap and cell **12b** with a band gap between the other two, if light enters the semiconductor
- 15 material from the bottom. The n-type layers of semiconductor material are characterized by low light absorption and high conductivity. The thickness of the band gap adjusted layers of intrinsic material may be in the range of 800 to 5,000 angstroms. The thickness of the n-type and p-type layers may be in the range of 25 to 400 angstroms.

- The foregoing is provided for purposes of explaining and disclosing preferred
- 20 embodiments of the present invention. It will be apparent to those skilled in the art that variations and modifications of the present invention can be made without departing from the scope or spirit of the invention. For example, variations in the transfer of the sodium cations after collection, variations in the route of the belt, different sources of electrical

energy, different sources of aqueous sodium chloride solution and variations in the conduit system for the chlorine gas and sodium hydroxide will be apparent to those skilled in the art. These changes and others may be made without departing from the scope or spirit of the invention in the following claims.